

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



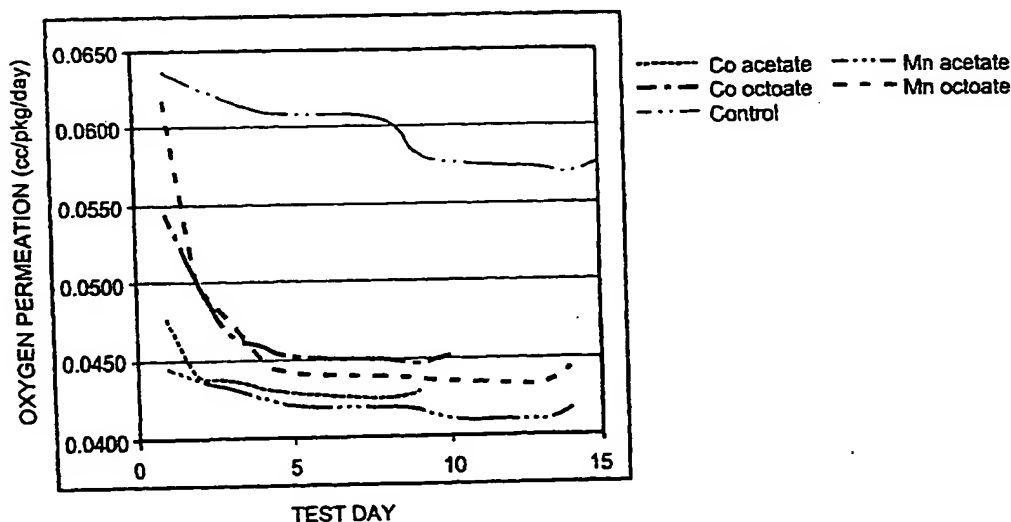
(43) International Publication Date
3 May 2001 (03.05.2001)

PCT

(10) International Publication Number
WO 01/30900 A1

- (51) International Patent Classification⁷: C08K 5/00, B65D 1/02, C08L 67/00
- (21) International Application Number: PCT/US00/29589
- (22) International Filing Date: 27 October 2000 (27.10.2000)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
09/427,788 27 October 1999 (27.10.1999) US
- (71) Applicant: THE COCA-COLA COMPANY [US/US];
One Coca-Cola Plaza, NW, Atlanta, GA 31313 (US).
- (72) Inventor: RULE, Mark; 2003 Royal Court, Atlanta, GA
30341 (US).
- (74) Agents: BIRCH, Anthony, L.; Finnegan, Henderson,
Farabow, Garrett & Dunner, L.L.P., 1300 I Street, NW,
Washington, DC 20005-3315 et al. (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— With international search report.
— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR REDUCTION OF ACETALDEHYDE AND OXYGEN IN BEVERAGES CONTAINED IN POLYESTER-BASED PACKAGING



(57) Abstract: A process for reducing acetaldehyde concentration in beverages contained in polyester-based packaging, wherein oxygen permeation into the container is reduced or eliminated. The polyester contains an oxidation catalyst active for the oxidation of acetaldehyde to acetic acid. A composition comprising a polyester and said oxidation catalyst. A polyester-based container comprising said oxidation catalyst, and a bottled beverage having a polyester-based container comprising an oxidation catalyst active for the oxidation of acetaldehyde to acetic acid.

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an adequate oxygen barrier; and those where off-taste from acetaldehyde is an issue, such as with water.

A number of foods and beverages are sensitive to oxygen. Some, such as beer, develop an off-taste when exposed to as little as 1 ppm of oxygen. Others, such as citrus products, lose their vitamin C potency due to reaction of ascorbic acid with oxygen. In the past, oxygen ingress into plastic containers has been addressed by the use of multi-layer containers containing barrier layers or scavenger layers. However, this approach is expensive, and compromises the transparency and recyclability of the plastic container.

Acetaldehyde is naturally formed during processing of any polyester containing ethylene glycol linkages. The compound is formed via a two-step reaction: the first step is cleavage of a polymer chain, generating a vinyl end group and a carboxylic acid end group. The second step is reaction of the vinyl end group with a hydroxyethyl end group, reforming the polymer chain and releasing acetaldehyde. Once formed, the acetaldehyde will migrate from the container sidewall into the beverage over time.

During the lifetime of a typical PET container, several hundred ppb of acetaldehyde can migrate from the container sidewall into the beverage. For sensitive products, such as water, these levels of acetaldehyde are significantly above the taste threshold. Approaches to address this problem have included the use of low molecular weight PET resin, to minimize the thermal history and hence acetaldehyde generation of the polymer, and the use of amine-based acetaldehyde scavengers. These approaches have been only partially effective. The use of low molecular weight resins compromise the mechanical strength and performance of the polyester. The use of acetaldehyde scavengers compromise the clarity and color of the polymer; in addition, the amount of acetaldehyde scavenger required is significant, and increase the cost of the polyester containers considerably.

alcohol, and is added to the polyester during the injection or extrusion molding process.

The present invention also relates to a polyester based container comprising an oxidation catalyst located within the polyester, wherein the oxidation catalyst is active for the oxidation of acetaldehyde to acetic acid.

The present invention is also related to a bottled beverage comprising a polyester-based container, a beverage in the container and an oxidation catalyst located within the polyester, wherein the oxidation catalyst is active for the oxidation of acetaldehyde to acetic acid.

The present invention further relates to a composition comprising a polyester and an oxidation catalyst, wherein the oxidation catalyst is active for the oxidation of acetaldehyde to acetic acid. The polyester may be polyethylene terephthalate or polyethylene naphthalate.

Although cobalt and manganese salts are widely used in polyesters as toners and transesterification catalysts, they are always present in the final polyester in a deactivated state. This deactivation is intentional, and is accomplished by the addition of phosphates, which react with the metal salts to form inactive, particulate metal phosphates. Therefore, such polyester compositions described in the prior art are outside of the present invention.

Other inventions have described the use of oxidation catalysts to prevent oxygen ingress into polyester containers. However, these prior inventions rely on the use of the oxidation catalyst to oxidize a readily oxidizable polymer that has been incorporated into the polyester container. Such oxidizable polymers include blends of PET with polybutylene and PET with partially aromatic nylons. These two polymers are readily oxidized by air in the presence of cobalt salts. However, use of these polymers is detrimental because of cost, processing difficulties, and the formation of undesirable reaction by-products. Because of the potential for migration of unknown oxidation products into the beverage, the

to acetic acid. The oxidation occurs by consumption of oxygen ingressing into the container sidewall, and thus, oxygen permeation into the polyester-based container is reduced or eliminated. The present invention also encompasses a polyester based container comprising an oxidation catalyst located within the polyester wherein the oxidation catalyst is active for the oxidation of acetaldehyde to acetic acid. In addition, the present invention relates to a bottled beverage comprising the polyester-based container described hereinbefore and a beverage in the container. The present invention further relates to a composition comprising a polyester and an oxidation catalyst, wherein the oxidation catalyst is active for the oxidation of acetaldehyde to acetic acid.

Although all oxidation catalysts active for the oxidation of acetaldehyde to acetic acid are contemplated in this invention, particularly useful catalysts include compounds comprising a variable valent metal such as cobalt or manganese salts. These catalysts can be present as simple salts, or as complexes with amines, phosphines, or alcohols. Preferred complexes include amines such as ethylenediaminetetraacetic acid (EDTA), glycine, and the like. Simple salts can include cobalt acetate, cobalt octoate, cobalt naphthenate, manganese acetate, manganese octoate, and manganese naphthenate. Other catalysts that may be effective include, but are not limited to nickel, vanadium, chromium, platinum, palladium, rhodium, silver, and copper.

The amount of oxidation catalyst added to the polyester is dependent upon the type of polyester used, the type of oxidation catalyst used, and the type of article being produced. Generally, the oxidation catalyst is present in the amount of approximately 1-500 ppm. Preferably, the polyester is present in the amount of approximately 5-50 ppm. Lesser amounts of oxidation catalyst result in reduced rates of oxygen and acetaldehyde consumption, and higher amounts lead to increased numbers of undesirable side reactions. The amount of oxidation catalyst can be

potential for the deactivation of the catalyst by reaction with other components of the polyester, especially phosphates.

The oxidation catalyst is activated by exposure to UV radiation, by exposure to peroxides, and by exposure to ozone. Exposure
5 to peroxides occur naturally in the course of processing PET due to the presence of small amounts of peroxy oxidation products, formed by the interaction of oxygen with diethylene glycol units in the polymer. Once active, the reaction process continually reactivates the catalyst.

The present invention is useful in preventing the migration of
10 acetaldehyde from polyester containers into any type of beverage in order to prevent off-taste of the beverage from occurring. Depending upon the type of beverage being used, the taste threshold of acetaldehyde may vary. However, it is preferred that the concentration of acetaldehyde in the beverage be decreased to approximately less than 40 ppb. More
15 preferably, the concentration of acetaldehyde in the beverage is decreased to less than 20 ppb.

Acetic acid has a much higher taste threshold than acetaldehyde, and is only detectable by taste at a concentration level approximately 1,000 times higher than the detectable concentration of
20 acetaldehyde. Thus, acetic acid may be present in the beverage in the amount of approximately 40 ppm or less. Preferably, the concentration of acetic acid in the beverage is less than 20 ppm.

As indicated above, the present invention may be used to improve the taste of any type of beverage including, but not limited to
25 water, colas, sodas, alcoholic beverages, juices, etc. However, it is particularly useful for preventing the off-taste of sensitive products such as water.

In another embodiment of the present invention, a bottled beverage is provided in a polyester-based container, wherein the
30 polyester-based container comprises an oxidation catalyst active for the oxidation of acetaldehyde to acetic acid.

In each example, the permeation rate of oxygen was determined by utilizing a Mocon OX-TRAN permeation measurement instrument. To measure oxygen ingress, each PET container was mounted on the OX-TRAN. The outer surface of the container was exposed to air at ambient temperature and humidity, while the inside of the container was continually swept with oxygen-free nitrogen at a rate of 10 to 20 cc/min. The sweep gas was then passed through a coulometric sensor, which electrochemically measured the amount of oxygen present in the sweep gas. From the detector response, the oxygen ingress rate was calculated.

The results of the analysis performed in Examples 2-6 are illustrated in the graph of Figure 1.

As the data in Fig. 1 indicates, the permeation of oxygen into bottles containing an oxidation catalyst was significantly lower than oxygen permeation into a bottle containing no oxidation catalyst.

Examples 7-9 are directed to acetaldehyde migration from PET containers into water.

Example 7

The acetaldehyde concentration in preforms comprising varying amounts of oxidation catalysts was determined. Specifically, preforms comprising 10 ppm, 25 ppm, and 50 ppm of cobalt octoate and preforms comprising 10 ppm, 25 ppm, and 50 ppm of cobalt naphthenate were tested. A preform comprising no oxidation catalyst was also tested as a control. To determine the acetaldehyde content in each preform, a portion of the preform was removed and chilled in liquid nitrogen. The preform sample was then ground to pass through a 2 mm screen. 0.100 grams of the granules were weighed into a 20 ml widemouth vial, and the vial was sealed with a teflon-lined crimp seal. The sample was then heated to 150 °C for 45 minutes to volatize the acetaldehyde contained in the polymer granules. The amount of volatized acetaldehyde was

more than once. The bottle tested was chilled to 4 °C, opened, and approximately 5 ml of carbonated water was removed via a pipette. The pipetted sample was then placed in a 20 ml vial containing approximately 1 gram of sodium chloride, and the amount of water added determined by weighing. The vial was then sealed, and heated to 75 °C for 30 minutes. A fixed amount of air in the headspace above the water was removed and analyzed by gas chromatography.

The results of the analysis performed in examples 7-9 are set forth in the table of Figure 2.

FIGURE 2
Concentration of Acetaldehyde
in PET Containers

Additive	Preform (ppm)	Headspace (ppm)	Beverage (ppb)				
			40 days	115 days	159 days	196 days	211 days
Control	5.71	3.19	39.6	112.0	117.0	137.0	162.7
10 ppm Co Octoate	10.91	5.98	40.2	87.6	98.0	118.0	132.0
25 ppm Co Octoate	12.67	6.96	23.5	66.6	74.0	91.0	110.1
50 ppm Co Octoate	24.05	9.33	28.7	32.1	79.0	119.0	141.1
10 ppm Co Naphthenate	6.46	3.78	53.5	132.5	—	—	—
25 ppm Co Naphthenate	7.56	3.70	25.0	51.5	79.0	107.0	126.5
50 ppm Co Naphthenate	11.38	5.28	81.1	98.5	—	—	—

According to Fig. 2, the presence of oxidation catalysts in PET containers at concentrations of 25 ppm or more, significantly inhibited the migration of acetaldehyde into the water. Cobalt octoate was most effective in preventing acetaldehyde migration at a concentration of 25 ppm with a 36% decrease in acetaldehyde concentration. Cobalt naphthenate was also most effective at 25 ppm, with a 32% decrease in acetaldehyde concentration.

We claim:

1. A method of reducing the amount of acetaldehyde in a beverage in a polyester-based container, the method comprising:
5 incorporating an oxidation catalyst into the polyester, wherein the oxidation catalyst is active for the oxidation of acetaldehyde to acetic acid.
- 10 2. The method of Claim 1, wherein the permeation of oxygen into the polyester-based container is reduced.
3. The method of Claim 1, wherein the polyester-based container is a polyethylene terephthalate container.
- 15 4. The method of Claim 1, wherein the oxidation catalyst is a cobalt or a manganese salt.
5. The method of Claim 1, wherein the oxidation catalyst
20 is a compound comprising an amine, a phosphine or an alcohol complexed with a variable valent metal.
6. The method of Claim 1, wherein the oxidation catalyst is added to the polyester during injection or extrusion molding of the
25 container.
7. The method of Claim 1, wherein the oxidation catalyst is present in the polyester in the amount of 1-500 ppm.
- 30 8. The method of Claim 7, wherein the oxidation catalyst is present in the polyester in the amount of 5-50 ppm.

18. The bottled beverage of Claim 15, wherein the oxidation catalyst is a cobalt or a manganese salt.

19. The bottled beverage of Claim 15, wherein the
5 oxidation catalyst is a compound comprising an amine, a phosphine or an alcohol.

20. The bottled beverage of Claim 15, wherein the oxidation catalyst is added to the polyester during injection or extrusion
10 molding of the container.

21. The bottled beverage of Claim 15, wherein the oxidation catalyst is present in the polyester in an amount of 1-500 ppm.

22. The bottled beverage of Claim 21, wherein the
15 oxidation catalyst is present in the polyester in an amount of 5-50 ppm.

23. The bottled beverage of Claim 15, wherein the beverage is water.
20

24. The bottled beverage of Claim 15, wherein the concentration of acetaldehyde in the beverage is less than 40 ppb.

25. The bottled beverage of Claim 24, wherein the
25 concentration of acetaldehyde in the beverage is less than 25 ppb.

26. The bottled beverage of Claim 15, wherein the concentration of acetic acid in the beverage is less than 40 ppm.

27. The bottled beverage of Claim 26, wherein the
30 concentration of acetic acid in the beverage is less than 25 ppm.

37. The polyester-based container of Claim 28, wherein the concentration of acetaldehyde in the beverage is less than 40 ppb.

5 38. The polyester-based container of Claim 37, wherein the concentration of acetaldehyde in the beverage is less than 25 ppm.

39. The polyester-based container of Claim 28, wherein the concentration of acetic acid in the beverage is less than 40 ppm.

10 40. The polyester-based container of Claim 39, wherein the concentration of acetic acid in the beverage is less than 25 ppm.

41. A composition comprising:
15 a polyester; and
 an oxidation catalyst wherein the oxidation catalyst is active for the oxidation of acetaldehyde to acetic acid.

42. The composition of Claim 41, wherein the polyester is
20 polyethylene terephthalate, polyethylene naphthalate, or a PET/PEN blend.

43. The composition of Claim 41, wherein the oxidation catalyst is a cobalt or a manganese salt.

25 44. The composition of Claim 41, wherein the oxidation catalyst is a compound comprising an amine, a phosphine or an alcohol.

45. The composition of Claim 41, wherein the oxidation
30 catalyst is present in the amount of 1-500 ppm.

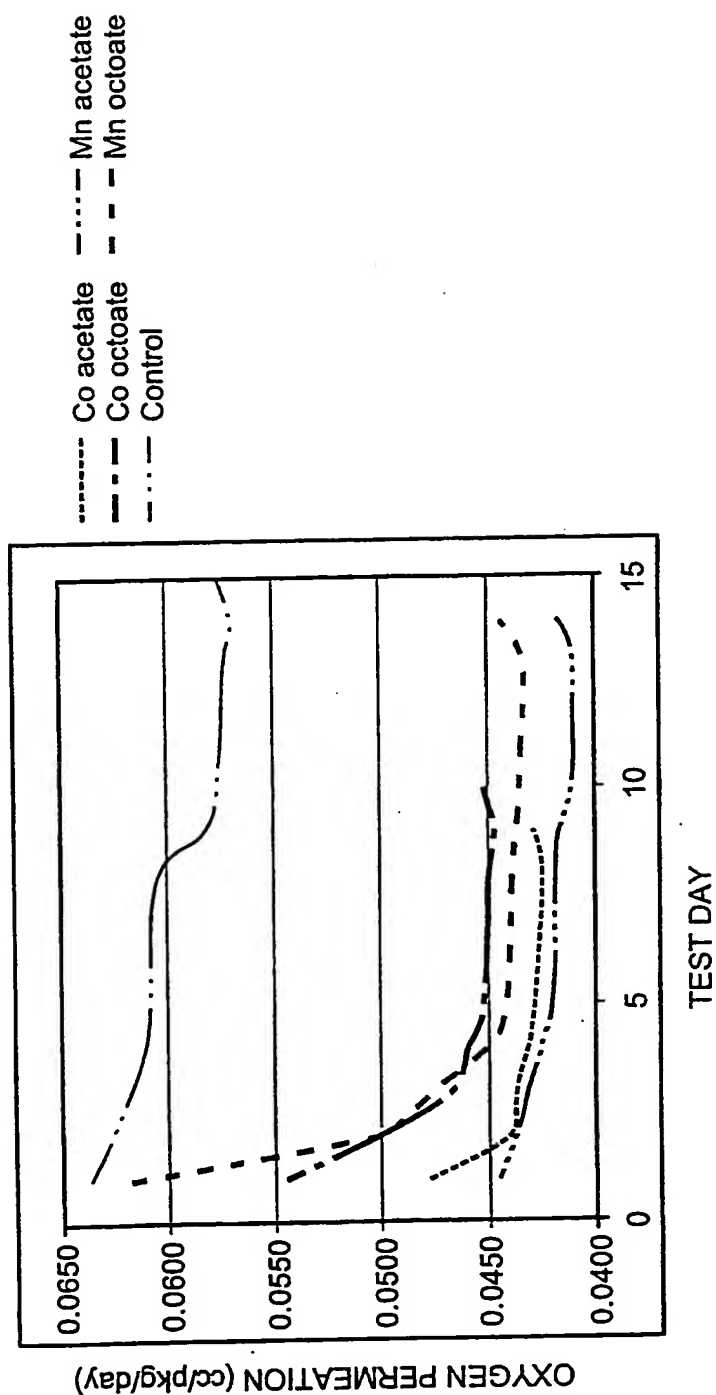


FIG. 1

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/29589

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 017 680 A (SUBLETT BOBBY J) 21 May 1991 (1991-05-21) column 1, line 55 -column 2, line 16; claim 1; table 1 column 3, line 26 -column 4, line 36 -----</p>	1-46
A	<p>US 4 820 795 A (HIRATA SADA0 ET AL) 11 April 1989 (1989-04-11) column 1, line 60 -column 2, line 10; examples -----</p>	1-46